



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 137 545
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 84201298.1

(51) Int. Cl.4: C 08 L 71/04

(22) Date of filing: 10.09.84

C 08 J 7/04, C 08 J 5/12
//(C08L71/04, 63:00)

(30) Priority: 12.10.83 NL 8303497

(71) Applicant: GENERAL ELECTRIC COMPANY
1 River Road
Schenectady New York 12305(US)

(43) Date of publication of application:
17.04.85 Bulletin 85/16

(72) Inventor: van der Meer, Roelof
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)

(84) Designated Contracting States:
DE FR GB IT NL

(74) Representative: Grever, Frederik
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)

(54) Articles manufactured wholly or partly from a polymer mixture and comprising a lacquer layer or an adhesive layer.

(57) The invention relates to articles manufactured from a polymer mixture which comprises a polyphenylene ether. The articles comprise a layer of lacquer or adhesive. If the articles are manufactured from a polymer mixture which moreover comprises an epoxy compound, a better bonding to the layer of lacquer or adhesive is obtained. This applies in particular when a polyurethane- or alkyd/melamine lacquer is used as a lacquer or a polyurethane- or epoxy adhesive is used as an adhesive.

EP 0 137 545 A2

General Electric Company, Schenectady, New York, U.S.A.
Applicant mentions as inventor: Roelof van der Meer.

Article manufactured wholly or partly from a polymer mixture and comprising a lacquer layer or an adhesive layer.

5 The invention relates to an article from a polymer mixture which comprises a polyphenylene ether, optionally a polystyrene or a rubber-modified polystyrene, and is provided with a lacquer layer or an adhesive layer.

10 Articles manufactured from a polyphenylene ether and having a polyurethane lacquer layer are known from French Patent Application 2,293,892. The known articles are manufactured from a polyphenylene ether
15 without any further additions. In such articles a good adhesion between the polyurethane lacquer or adhesive layer is of importance.

20 The invention provides articles having a good adhesion between the lacquer layer or adhesive layer and the actual article.

25 In particular, the invention provides articles having a lacquer layer on the basis of a polyurethane or an alkyd/melamine or having a polyurethane- or epoxy adhesive layer.

30 The article according to the invention is characterized in that it is manufactured from a polymer mixture comprising a polyphenylene ether and a epoxy compound.

0137545

8-CB-10.124

-2-

Polymer mixtures comprising a polyphenylene ether, optionally a polystyrene or a rubber-modified polystyrene and an epoxy compound, are known per se from Japanese Patent Application 45/120514 laid open
5 to public inspection under No. 48/39017.

Chemical Abstract, Vol. 81, no. 20, November 1974, number 122,066 u describes an adhesive composition containing poly(phenylene oxide) and an epoxy resin having good adhesion to copper foils. The composition is adhered to the copper foil at elevated temperature (300°C) and pressure (50 - 100 kg/cm³).
10

It is furthermore known from German Patent Application 30.39201 that the adhesion of polyurethane foam to articles formed from a polyphenylene ether-polystyrene mixture can be improved by the addition of a special impact-proof modified polystyrene as described in German Patent Application 25 25 019.
15

A good adhesion with lacquers and adhesives can be obtained when the article is manufactured from a polymer mixture which in addition comprises a block copolymer having blocks derived from a conjugated diene
20 and from a vinyl aromatic compound. This applies in particular to the adhesion with lacquers, for example, polyurethane lacquers and alkyd/melamine lacquers.
25

The articles according to the invention are manufactured from a polymer mixture comprising the following constituents:
30

- A. a polyphenylene ether;
- B. an epoxy compound.

This polymer mixture may furthermore comprise:

- C. a saturated or unsaturated block copolymer;
- D. a polystyrene or a rubber-modified polystyrene;
- E. usual additives for polymer mixtures comprising a polyphenylene ether.

5

A. Polyphenylene ether.

Polyphenylene ethers and their preparation are described in numerous patent publications, for example, 10 in United States Patents 3,306,874; 3,306,875; 3,257,357 and 3,257,358. The polymer mixture according to the invention may comprise one or more of all the known polyphenylene ethers, notable also homopolymers, copolymers and graft copolymers. The polyphenylene 15 ether in the polymer mixtures according to the invention preferably comprises units derived from 2,6-dimethylphenol.

B. Epoxy compound.

20 The following compounds may be used as an epoxy compound:

- (1) Epoxide resins which are prepared by condensing phenols having two or more OH-groups with epichlorohydrin in various ratios.
- 25 (2) Epoxide resins which are prepared by condensing alcohols having two or more OH-groups (= poly alcohols) with epichlorohydrin.
- (3) Glycidyl ethers derived from phenols or alcohols having one OH-group.
- 30 (4) Glycidyl ethers derived from amine compounds.
- (5) Epoxidized higher olefins or cycloalkanes.

Typical examples of epoxide resins mentioned B (1) are the condensation products of bisphenol A or 35 bisphenol F with epichlorohydrin (for example, Araldit

0137545

8-CB-10.124

-4-

GT 7071, Araldit GY 266 and Araldit GT 6099 of Ciba Geigy), condensation products of resorcinol and epichlorohydrin, condensates of tetrabromobisphenol A and epichlorohydrin and the glycidyl ether products of phenol Novolak or kresol Novolak, for example Ciba EPN 138 of Ciba Geigy. Condensates of phenols having two OH-groups and epichlorohydrin having a reasonably high molecular weight, for example the phenoxy resins produced by Union Carbide Corp., may also be used.

10

As examples of the epoxide resins mentioned B (2) may be stated the condensates of ethylene glycol, propylene glycol, butylene glycol, polyethylene glycol, glycerin, trimethylol ethane, trimethylol propane, or pentaerythritol with epichlorohydrin.

15 As examples of the glycidyl ether products B (3) may be mentioned phenyl glycidyl ether, n-butyl glycidyl ether, cresyl glycidyl ether, and 2-ethylhexyl glycidyl ether.

20 As an example for B (4) is mentioned a diglycidyl ether derived from aniline.

25

As an example of the compounds mentioned B (5) may be stated epoxidized unsaturated oils, for example, soya bean oil and linseed oil (Edenol D 81 and Edenol B 316, respectively, of Henkel).

30

Due to the small plasticizing effect in polymer mixtures comprising a polyphenylene ether, epoxy resins having a molecular weight of more than 1,000 are preferably used.

8-CB-10.124

-5-

C. Saturated or unsaturated block copolymer.

Block copolymers which may be used in the polymer mixtures: block copolymers of the type A-B, A-B-A' or also radial teleblock copolymers and so-called tapered block copolymers, i.e. block copolymers in which copolymers of the conjugated diene and the vinyl aromatic compound are present between the blocks. The block built up from the conjugated diene in all the types of block copolymers considered here may be fully or partly hydrogenated, in which case saturated block copolymers are obtained. In the block copolymers A-B and A-B-A', B consists of a block of a conjugated diene, for example, butadiene, isoprene or pentadiene-1,3, and blocks A and A' consist of vinyl aromates, for example, styrene, alpha-methylstyrene, vinyl toluene, vinyl xylene and/or vinyl naphtalene. B preferably consists of polybutadiene and A and A' preferably consist of polystyrene. Radial teleblock copolymers are to be understood to mean brancsal urbzjanf sigtex cbroyf which are formed by a polymer of a conjugated diene, preferably butadiene, blocks of a vinyl aromatic compound, preferably styrene and a coupling agent. In this copolymer structure, various chains of the diene polymer, usually three or more, start from a coupling agent in which each chain at its other end comprises a block of the aromatic vinylpolymer. All the said block copolymers are known per se.

D. Polystyrene or rubber-modified polystyrene.

As a polystyrene there may be used a compound which contains more than 25% of units of a compound of the formula R-C(C₆H(5-p)Z_p) = CH₂, wherein R is a hydrogen atom, a lower alkyl group (having, for example, 1-6 carbon atoms) or a halogen atom, Z is a hydrogen atom or a chlorine atom or a lower alkyl group or a vinyl group and p = 0 or an integer from 1 to 5.

8-CB-10.124

-6-

Suitable polystyrene compounds and suitable rubber-modified polystyrene compounds (high-impact polystyrene) are homopolymers, for example, polystyrene itself, polychlorostyrene and poly-alpha-methyl styrene, rubber-modified polystyrenes, for example, the commercially available high-impact polystyrene polymers and also the styrene-containing copolymers, for example, styrene acrylonitrile copolymers, styrene butadiene copolymers, styrene acrylonitrile-butadiene terpolymers, copolymers of ethylvinylbenzene and divinylbenzene and the like.

When the polymer mixture includes a polystyrene or a rubber-modified polystyrene, the ratio between the quantity by weight of polyphenylene ether and polystyrene may be varied within wide limits, for example, between 1:4 and 20:1.

E. Usual additives for polymer mixtures of polyphenylene ether.

Examples of usual additives are dyes and pigments, agents to make the polymer mixture antistatic, agents to give the polymer mixture better flame-retarding properties, stabilizers, fillers, reinforcing fibres and mineral oil.

The articles according to the invention are manufactured according to usual techniques of processing synthetic resins, for example, by injection moulding, extrusion and the like. Layers of lacquer or adhesive on the basis of a polyurethane may be provided on the articles. Lacquers on the basis of an alkyd/melamine system or epoxy adhesives may also be provided.

Polyurethane lacquers or adhesives are to be understood to mean lacquers or adhesives which comprise urethane groups in the ultimate protective layer or in the ultimately formed compound. Urethane groups are 5 formed by the reaction of an active hydrogen atom of a hydroxyl group with an isocyanate group.

In most cases a polyurethane lacquer or adhesive consists of two components which are mixed with 10 each other immediately before use. The two components are usually a prepolymer with isocyanate end groups and a resin with reactive OH-groups. In Verfkroniek, 43 (1970), p. 269-276 are mentioned as examples of suitable reactive resins:

- 15 a. polyacrylate-polyol
- b. polyester-polyol
- c. polyether-polyol

The OH-value of the lacquer or adhesive determines the ultimate degree of cross-linking of the 20 lacquer or adhesive. The lacquer or adhesive usually comprises one or more of the following solvents: ethyl acetate, butyl acetate, toluene and xylene.

Alkyd/melamine lacquers are baking enamels. By 25 raising the temperature (baking), curing takes place. The two components, on the one hand the alkyd resin with free carboxyl groups and on the other hand the melamine resin with free OH-groups, are supplied as one 30 system.

Suitable epoxy adhesives are two-components systems which are mixed immediately before use. The main component is an epoxy resin having a given epoxy 35 equivalent number, while the second component, "the

hardener", ensures curing by reaction with the epoxy group.

In the examples hereinafter, thin, disk-shaped plates are formed by injection moulding from the polymer mixtures mentioned therein. Lacquer layers and/or adhesive layers on the basis of a polyurethane are provided on said plates. The bonding between the polyurethane lacquer layer - if not otherwise stated - is determined according to the so-called "Gitterschnittprüfung von Anstrichen und ähnlichen Beschichtungen" (cross-cut test on paint coatings and similar coatings) according to DIN 53 151. The tests have been carried out with an Ericsen type 295 testing apparatus. By means of said testing apparatus, a pattern of squares is scratched in the coating layer. An adhesive tape is adhered across said pattern; the tape is thoroughly pressed on. The adhesive tape is then pulled off. The appearance of the square pattern is then evaluated visually. With an evaluation Gt0 the coating layer is still fully intact. With an evaluation Gt5 more than 65% of the surface of the diamond pattern has worked loose. With intermediate evaluations Gt1, Gt2, Gt3, Gt4 a result getting worse and worse in this sequence is obtained.

The bonding of the adhesive layer is determined as follows. A standardized tensile test bar is manufactured from the polymer mixtures by injection moulding. A PVC-foil is adhered to the tensile test bar by means of adhesive (example III). The adhesive is cured. The peel resistance is then determined (N/mm). The peel resistance is defined as the average force per length unit of the bonding line to further pull apart the two parts bonded together once the peeling has

started. For this method of determining the peel resistance there may be referred to International Standard ISO 4578-1979 (E) and to DIN 53 282. In example IV the bonding of the adhesive is determined by adhering 5 two tensile test bars together with an overlap of 1 cm. The force necessary to slide the tensile test bars parallel to each other is then measured as the peel resistance (N/mm^2).

10 Example I

Polymer mixtures were prepared (samples A, B and C) having a composition as stated in Table I hereinafter. From these mixtures, thin disc-shaped plates were manufactured by injection moulding. The plates 15 were lacquered under different conditions with three commercially available polyurethane lacquers by means of a spray gun. The bonding between the plates and the lacquer layer was determined after seven days according to the "Gitterschnittprüfung" (cross-cut test) (DIN 20 53151). The lacquer conditions and the results obtained are recorded in Tables II, III, IV, V and VI herein after. The tests were always carried out in quintuplicate.

25

30

35

0137545

8-CB-10.124

-10-

Table I

(composition parts by weight)

5	Sample	A	B	C
	Poly(2,6-dimethyl-1,4-phenylene ether)	44	40	53
	High-impact polystyrene	56	51	38
10	ZnO + ZnS	0.3	0.3	0.3
	Organic phosphite	0.7	0.7	0.7
	Block copolymer ¹	-	6.5	6.5
	Epoxy compound ²	-	2.5	2.5
15	1) a block copolymer of the type A-B-A', wherein A and A' are polystyrene blocks and B is a non-hydrogenated polybutadiene block, obtainable under the trademark Cariflex TRKX-65			
	2) an epoxy compound in the form of a solid epoxide resin on the basis of bisphenol A, obtainable under the trademark Araldit GT 7071.			
20				

Table II

25	Conditions upon spraying the polyurethane lacquer.
	- distance spray gun-substrate 0.3 m
	- pressure in spray gun 0.3 megapascal (MPa)
	- temperature substrate 30° C
30	- curing lacquer 30 minutes at 80° C

0137545

8-CB-10.124

-11-

Results:

	Sample	Lacquer I ³	Lacquer II ⁴
5	A	1 x GT4; 4 x Gto	5 x Gto
	B	5 x Gto	5 x Gto
	C	5 x Gto	5 x Gto

3) and 4) see note below Table VI

10

Table III

Conditions upon spraying the polyurethane lacquer

	- distance spray gun-substrate	0.6 m
15	- pressure in spray gun	0.4 megapascal (MPa)
	- temperature substrate	30° C
	- curing lacquer	30 minutes at 80° C

Results:

	Sample	Lacquer I ³	Lacquer II ⁴
20	A	5 x Gt4	1 x Gt2; 4 x Gto
	B	5 x Gto	5 x Gto
	C	5 x Gto	5 x Gto

25 3) and 4) see note below Table VI

Table IV

30 Conditions upon spraying the polyurethane lacquer

	- distance spray gun-substrate	0.6 m
	- pressure in spray gun	0.4 megapascal (MPa)
	- temperature substrate	20° C
	- curing lacquer	30 minutes at 80° C

35

0137545

8-CB-10.124

-12-

Results:

	Sample	Lacquer I ³	Lacquer II ⁴
A		5 x Gt4	4 x Gt2
B		5 x Gt4	5 x Gto
5 C		5 x Gt4	5 x Gto

3) and 4) see note below Table VI

Table V

10

Conditions upon spraying the polyurethane lacquer

As in Example IV, with the exception of:

- curing lacquer 30 minutes at 120° C

15

Results:

Sample	Lacquer I ³
A	5 x Gto
B	5 x Gto
C	5 x Gto

20

3) see note below Table VI

Table VI

25

Conditions upon spraying the polyurethane lacquer

- distance spray gun-substrate 0.6 m
- pressure in spray gun 0.6 megapascal (MPa)
- temperature substrate 35° C
- curing lacquer 30 minutes at 80° C

30

Results:

Sample	Lacquer I ³	Lacquer II ⁴
A	5 x Gt4	4 x Gt2/3; 1xGto
B	5 x Gt4	5 x Gto
35 C	5 x Gt4	5 x Gto

0137545

8-CB-10.124

-13-

3. Lacquer I is a two components polyacrylate-polyol/isocyanate having an OH-value of 4%, commercially available as "Autocryl" from Messrs. Sikkens.
4. Lacquer II is a two components polyacrylate-polyol/isocyanate lacquer having an OH-value of 4%, commercially available as "Cellioster 1834" from Messrs. La Celliose.

10 It appears from the Tables that the conditions upon spraying the lacquers are of importance for the resulting bonding. In practice, however, it is of essential importance that a good bonding should also be obtained in less optimum conditions.

15 It appears from the Tables that with the samples B and C according to the invention a better or equal result is obtained as with sample A (reference sample).

20 Example II.

Two polymer mixtures were prepared corresponding to samples A and B of Table I. Disk-shaped plates were manufactured from the polymer mixture by means of injection moulding. The plates were 25 lacquered with a polyurethane lacquer under different conditions. As a polyurethane lacquer was used a two-components polyacrylatepolyol/isocyanate lacquer obtainable as "Cellioster 2400 Alu Nacre 3387 HU" from La Celliose.

30

All experiments were carried out in quintuplicate. The bonding strength was determined according to the "Gitterschnitt" test. Moreover the impact strength prior to and after painting was determined 35 according to the so-called "falling dart impact" test

0137545

8-CB-10.124

-14-

(thickness disk 3.2 mm; falling height 2.15 m; mass 10.378 kg). The results are recorded in Table VII.

5

Table VII

		Sample A	Sample B
	Properties before painting "Falling		
10	dart impact strength" (J)	60	95
	Condition used upon spraying the poly- urethane lacquer	"Gitterschnitt" value	"Gitterschnitt" value cross-cut
15	I distance spray gun- substrate 0.3 m; pressure in spray gun 0.3 mega- pascal; temperature	5 x Gt0	5 x Gt0
20	surface 20°C; curing lacquer 30 min. at 80°C		
25	II distance spray gun- substrate 0.6 m; pressure 3 x Gt2 in spray gun 0.6 mega- pascal; temperature surface 20°C; curing lacquer 30 min. at 80° C	1 x Gt0 1 x Gt4	5 x Gt0
30			

0137545

8-CB-10.124 -15-

III distance spray gun-
substrate 0.6 m; pressure
in spray gun 0.6 mega-
pascal; temperature 5 x Gt4 5 x Gto
5 surface 35°C; curing
lacquer 30 min. at
80° C

Properties after painting
10 according to II. "Falling
dart impact strength" (J) 10 50

It may be seen from Table VII that sample B
according to the invention shows a better or equal
15 bonding with polyurethane lacquer than sample A
(reference sample).

Example III.

Three polymer mixtures were manufactured with
20 the composition as stated hereinafter in Table VIII.

Table VIII
(Compositions in parts by weight)

Sample	D	E	F
25 poly(2,6-dimethyl- 1,4-phenylene ether)	32	32	32
30 high-impact polystyrene	64	64	64
ZnO + ZnS	0.3	0.3	0.3
organic phosphite	0.9	0.9	0.9
35 block copolymer ¹	5	5	5
epoxy compound ²	-	3	6

8-CB-10.124

-16-

1) and 2): In this example the same blockcopolymer and the same epoxy compound were used as indicated in Example I, Table I.

5 Standardized rods for a tensile test were manufactured from the resulting polymer mixtures by injection moulding. A PVC foil was adhered to the rods by means of a polyurethane adhesive, namely a two-components polyurethane adhesive of the tradename
10 "Hernerts 7550". The glued joint was heated at 80° C for 5 minutes. After 5 days the peel resistance was determined. The results are recorded in Table IX hereinafter.

15

Table IX.

Sample

D

E

F

Average peel resistance

20 (three measurements)

N/mm 2.8+0.05^a) 3.6+0.1^a) 3.7+0.1^a)

a) Standard deviation.

25 Example IV.

A large number of tensile test bars were formed (injection moulded) from each of the polymer mixtures according to samples A, B and C of Example I. Always two rods from the same polymer mixture were bonded together with an overlap of 1 cm by means of a polyurethane adhesive or an epoxy adhesive. The adhesive was cured, partly at 20° C and partly at 80° C (60 minutes) and partly at 120° C (60 minutes). Two different polyurethane adhesives and one epoxy adhesive were used. Seven days after adhering the peel

0137545

8-CB-10.124

-17-

resistance was determined. Each test was repeated four times. The results obtained are recorded in Table X hereinafter.

5

Table X.

		Peel resistance (N/mm ²) after curing at		
	<u>Sample A</u>	20° C	80° C	120° C
10	Adhesive I ⁵	3;3;3;3	7;7;4;4	-
	Adhesive II ⁶	1;<1;<1;<1	3;2;1;1	6;6;5;4
	Adhesive III ⁷	2;2;2;1	2;2;<1;<1	-
15	<u>Sample B</u>			
	Adhesive I ⁵	4;3;3;2	7;9;3;3	-
	Adhesive II ⁶	3;2;2;2	4;3;3;3	4 x 10
	Adhesive III ⁷	3;3;3;2	8;8;8;5	-
20	<u>Sample C</u>			
	Adhesive I ⁵	6;5;4;4	>10;10;9;4	-
	Adhesive II ⁶	3;3;2;2	6;4;4;3	4 x >10
	Adhesive III ⁷	3;3;2;2	4;4;4;2	-
25	5) A two-components polyurethane adhesive commercially available under the trademark Bison from Perfekta.			
	6) A two-components polyurethane adhesive commercially available under the trademark Macroplast UK 8210 from Henkel.			
30	7) A two-components epoxy adhesive commercially available under the indication "XB-7838 B/A from 3M Company.			

0137545

8-CB-10.124

-18-

It may be seen from the Table that the samples B and C according to the invention provide a better or equal peel resistance as compared with Sample A (not according to the invention).

5

Example V.

Polymer mixtures (samples G, H, J and K) were prepared in a composition as indicated in Table XI hereinafter. Injection moulding, lacquering and determination of bonding were carried out as stated in Example I. The results obtained are recorded in Table XII.

15

Table XI.

(Composition parts by weight)

	<u>Sample</u>	G	H	J	K
20	Poly (2,6-dimethyl-1,4-phenylene ether)	44	44	44	44
	High-impact polystyrene	56	56	56	56
25	ZnO +ZnS	0.3	0.3	0.3	0.3
	Organic phosphite	0.8	0.8	0.8	0.8
	Block copolymer ¹	-	-	6.5	6.5
30	Epoxy compound ²	-	2.5	-	2.5

1) and 2) see Table I.

0137545

8-CB-10.124

-19-

Table XII.

			"Gitterschnitt" value		
	<u>Sample</u>	G	H	J	K
5	I Distance spray gun-substrate 0.45 m; pressure in spray gun=0.6 4xGt4 MPa; temperature substrate=35°C; curing lacquer 75 minutes at 80°C		4xGto	4xGt4	4xGto
10					
15	II Distance spray gun-substrate 0.6 m; pressure in spray gun=0.6 2xGt4 MPa; temperature substrate=20°C; curing 30 minutes at 120°C		2xGto	2xGto	2xGto
20					
25	III Distance spray gun-substrate 0.6 m; pressure in spray gun=0.6 3xGt4 MPa; temperature substrate=20°C; curing lacquer 30 minutes at 80°C		2xGt4	1xGt4	1xGt4
30			1xGto	2xGto	2xGto

0137545

8-CB-10.124

-20-

It appears from Table XII that under critical lacquer conditions the sample with the block copolymer shows a better or equal bonding than the reference sample, while the sample with only the epoxide compound 5 shows a better bonding, and the sample with both the block copolymer and the epoxide compound shows the best bonding.

Example VI.

10 Polymer mixtures were prepared having a composition as of sample A to which, however, 2.5 parts by weight of various epoxy compounds are added (Table XIII). The samples L, M, N and P were obtained in this manner (Table XIII). Injection moulding, lacquering and 15 bonding determination were carried out as stated in Example I. The bonding found is recorded in Table XIV.

Table XIII.
(Composition parts by weight)

20

	<u>Sample</u>	A	L	M	N	P
Epoxy compound:						
	Edenol B 35 ⁸	-	2.5	-	-	-
25	Edenol D 81 ⁹	-	-	2.5	-	-
	Edenol B 316 ¹⁰	-	-	-	2.5	-
	ERL 4221 ¹¹	-	-	-	-	2.5

8) Edenol B 35 is an isoalkyl epoxystearate of Henkel
30 9) Edenol D 81 is an epoxidized soya bean oil of
Henkel

0137545

8-CB-10.124 -21-

10) Edenol B 316 is an epoxidized linseed oil of Henkel

11) ERL 4221 is 3,4-epoxycyclohexylmethyl-3,4-epoxy-
cyclohexyl carboxylate and is marketed by Union
Carbide Corporation under the tradename Bakelite
5 Cycloaliphatic Epoxy Resin ERL 4221

Table XIV.

10	<u>Sample</u>	"Gitterschnitt" value				
		A	L	M	N	P
15	I Distance spray gun-substrate =0.6 m; pressure in spray gun=0.6 MPa; temperature substrate=35°C; 3xGt4 3xGto 3xGto 3xGto 3xGto curing lacquer 30 minutes at 20 80° C.					
25	II Distance spray gun-substrate =0.6 m; pressure in spray gun=0.6 MPa; temperature substrate=35°C; 3xGt4 2xGto 3xGto 2xGto 3xGto curing lacquer 1xGt2 1xGt2 30 minutes at 30 120° C.					

0137545

8-CB-10.124

-22-

Example VII.

Test plates were manufactured from polymer mixtures according to samples A and C of Example I. The samples were lacquered by spraying with two different 5 alkyd/melamine lacquers. The conditions during lacquering and the found bonding results are recorded in Table XV hereinafter.

10

Table XV.

"Gitterschnitt" value

Sample

A

C

Conditions during lacquering

15

-distance spray gun-

substrate 0.3 m.

-pressure in spray gun 0.3 MPa

-temperature substrate 20°C

20

-curing lacquer 30 minutes
at 80° C

Lacquer III¹²

2xGt4;1xGto

3xGto

Lacquer IV¹³

3xGt4

3xGt4

25

Conditions during lacquering

as above, but:

-curing lacquer 30 minutes
at 120° C

30

Lacquer III¹²

3xGt4

3xGto

Lacquer IV¹³

3xGt4

2xGt4;

0137545

8-CB-10.124

-23-

cont'd Table XV

Conditions during lacquering

-distance spray gun-

5 substrate 0.6 m

-pressure in spray gun 0.6 MPa

-temperature substrate 20°C

-curing 80°C

10 Lacquer III¹²

3xGt4

3xGto

Lacquer IV¹³

3xGt4

3xGt4

Conditions as above, but:

-curing 120°C

15

Lacquer III¹²

3xGt4

3xGt4

Lacquer IV¹³

3xGt4

3xGt4

12) An alkyd/melamine paint having a rather high carboxyl value, obtainable under indication C3E577 from Schaeppman Lakfabrieken.

20 13) An alkyd/melamine paint (code C4E34) having a free inorganic acid (code H4E15) of Schaeppman Lakfabrieken.

25

It may be seen from the results recorded in Table XV that a better or equal bonding is obtained with a polymer mixture according to the invention B than with polymer mixture A (reference sample).

30

35

CLAIMS:

1. An article manufactured wholly or partly from a polymer mixture comprising a polyphenylene ether, optionally a polystyrene or a rubber-modified poly-
5 styrene and comprising a lacquer layer or an adhesive, characterized in that the article is manufactured from a polymer mixture which comprises a polyphenylene ether and an epoxy compound.
2. An article as claimed in Claim 1, charac-
10 terized in that the article is manufactured from a polymer mixture which comprises in addition a saturated or unsaturated block copolymer having blocks derived from a conjugated diene and from a vinyl aromatic compound.
- 15 3. An article as claimed in Claims 1-2, charac-
terized in that the article is manufactured from a polymer mixture which, calculated with respect to the overall quantity of polyphenylene ether, optionally pre-
sent polystyrene or rubber-modified polystyrene,
20 optionally present block copolymer, comprises 0.2 to 7.5% by weight of epoxy compound and 0 to 25% by weight of block copolymer.
- 25 4. An article as claimed in Claims 1-3, charac-
terized in that the article is manufactured from a polymer mixture which comprises an epoxy compound having a molecular weight of more than 1,000.
- 30 5. An article as claimed in Claims 1-4, charac-
terized in that the article is manufactured from a polymer mixture which comprises a block copolymer having blocks derived from butadiene and from styrene the poly-
butadiene blocks of which may be hydrogenated.
- 35 6. An article as claimed in Claims 1-5, charac-
terized in that the article has a polyurethane- or alkyd/melamine lacquer layer or a polyurethane- or epoxy adhesive layer.



⑩ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 137 545
B1

⑫

EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: **01.07.87**

⑮ Int. Cl.⁴: **C 08 L 71/04, C 08 J 7/04,
C 08 J 5/12 // (C08L71/04,
63:00)**

⑯ Application number: **84201298.1**

⑯ Date of filing: **10.09.84**

④ Articles manufactured wholly or partly from a polymer mixture and comprising a lacquer layer or an adhesive layer.

⑩ Priority: **12.10.83 NL 8303497**

⑦ Proprietor: **GENERAL ELECTRIC COMPANY
1 River Road
Schenectady New York 12305 (US)**

⑩ Date of publication of application:
17.04.85 Bulletin 85/16

⑦ Inventor: **van der Meer, Roelof
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom (NL)**

⑩ Publication of the grant of the patent:
01.07.87 Bulletin 87/27

⑦ Representative: **Grever, Frederik
General Electric Plastics B.V. P.O. Box 117
NL-4600 AC Bergen op Zoom (NL)**

⑩ Designated Contracting States:

DE FR GB IT NL

⑩ References cited:

**FR-A-2 293 892
GB-A-1 561 140
GB-A-1 562 540**

**CHEMICAL ABSTRACTS, vol. 81, 1974, page 75,
no. 122066u, NEW YORK (US)**

EP 0 137 545 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

0 137 545

Description

The invention relates to an article from a polymer mixture which comprises a polyphenylene ether, optionally a polystyrene or a rubber-modified polystyrene, and is provided with a lacquer layer on an adhesive layer.

Articles manufactured from a polyphenylene ether and having a polyurethane lacquer layer are known from FR-A-2 293 892. The known articles are manufactured from a polyphenylene ether without any further additions. In such articles a good adhesion between the polyurethane lacquer or adhesive layer is of importance.

10 The invention provides articles having a good adhesion between the lacquer layer or adhesive layer and the actual article.

In particular, the invention provides articles having a lacquer layer on the basis of a polyurethane or an alkyd/melamine resin or having a polyurethane- or epoxy adhesive layer.

15 The article according to the invention is characterized in that it is manufactured from a polymer mixture comprising a polyphenylene ether and an epoxy compound.

The articles according to the invention are preferably manufactured from a polymer mixture which, calculated with respect to the overall quantity of polyphenylene ether, optionally present polystyrene or rubber-modified polystyrene, optionally present block copolymer, comprises 0.2 to 7.5% by weight of epoxy compound and 0 to 25% by weight of block copolymer.

20 Polymer mixtures comprising a polyphenylene ether, optionally a polystyrene or a rubber-modified polystyrene and an epoxy compound, are known per se from JP-A-45/120514 laid open to public inspection under No. 48/39017.

Chemical Abstract, Vol. 81, no. 20, November 1974, number 122,066 describes an adhesive composition containing poly(phenylene oxide) and an epoxy resin having good adhesion to copper foils.

25 The composition is adhered to the copper foil at elevated temperature (300°C) and pressure (50—100 kg/cm²).

It is furthermore known from DE-A-30 39201 that the adhesion of polyurethane foam to articles formed from a polyphenylene ether-polystyrene mixture can be improved by the addition of a special impact-proof modified polystyrene as described in DE-A-25 25 019.

30 A good adhesion with lacquers and adhesives can be obtained when the article is manufactured from a polymer mixture which in addition comprises a block copolymer having blocks derived from a conjugated diene and from a vinyl aromatic compound. This applies in particular to the adhesion with lacquers, for example, polyurethane lacquers and alkyd/melamine lacquers.

The articles according to the invention are manufactured from a polymer mixture comprising the following constituents:

- A. a polyphenylene ether;
- B. an epoxy compound.

This polymer mixture may furthermore comprise:

- C. a saturated or unsaturated block copolymer;
- D. a polystyrene or a rubber-modified polystyrene;
- E. usual additives for polymer mixtures comprising a polyphenylene ether.

A. Polyphenylene ether.

45 Polyphenylene ethers and their preparations are described in numerous patent publications, for example, in US-A-3 306 874; US-A-3 306 875; US-A-3 257 357 and US-A-3 257 358. The polymer mixture according to the invention may comprise one or more of all the known polyphenylene ethers, notably also homopolymers, copolymers and graft copolymers. The polyphenylene ether in the polymer mixtures according to the invention preferably comprises units derived from 2,6-dimethylphenol.

B. Epoxy compound.

The following compounds may be used as an epoxy compound:

- (1) Epoxide resins which are prepared by condensing phenols having two or more OH-groups with epichlorohydrin in various ratios.
- (2) Epoxide resins which are prepared by condensing alcohols having two or more OH-groups (=poly alcohols) with epichlorohydrin.
- (3) Glycidyl ethers derived from phenols or alcohols having one OH-group.
- (4) Glycidyl ethers derived from amine compounds.
- (5) Epoxidized higher olefins or cycloalkanes.

60 Typical examples of epoxide resins mentioned B (1) are the condensation products of bisphenol A or bisphenol F with epichlorohydrin (for example, Araldit GT 7071, Araldit GY 266 and Araldit GT6099 of Ciba Geigy), condensation products of resorcinol and epichlorohydrin, condensates of tetrabromobisphenol A and epichlorohydrin and the glycidyl ether products of phenol Novolak or kresol Novolak, for example Ciba EPN 138 of Ciba Geigy. Condensates of phenols having two OH-groups and epichlorohydrin having a

0 137 545

reasonably high molecular weight, for example the phenoxy resins produced by Union Carbide Corp., may also be used.

As examples of the epoxide resins mentioned B (2) may be stated the condensates of ethylene glycol, propylene glycol, butylene glycol, polyethylene glycol, glycerin, trimethylol ethane, trimethylol propane, or pentaerythritol with epichlorohydrin.

As examples of the glycidyl ether products B (3) may be mentioned phenyl glycidyl ether, n-butyl glycidyl ether, cresyl glycidyl ether, and 2-ethylhexyl glycidyl ether.

As an example for B (4) is mentioned a diglycidyl ether derived from aniline.

As an example of the compounds mentioned B (5) may be stated epoxidized unsaturated oils, for example, soya bean oil and linseed oil (Edenol D 81 and Edenol B 316, respectively, of Henkel).

Due to the small plasticizing effect in polymer mixtures comprising a polyphenylene ether, epoxy resins having a molecular weight of more than 1,000 are preferably used.

C. Saturated or unsaturated block copolymer.

Block copolymers which may be used in the polymer mixtures: block copolymers of the type A—B, A—B—A' or also radial teleblock copolymers and so-called tapered block copolymers, i.e. block copolymers in which copolymers of the conjugated diene and the vinyl aromatic compound are present between the blocks. The block built up from the conjugated diene in all the types of block copolymers considered here may be fully or partly hydrogenated, in which case saturated block copolymers are obtained. In the block copolymers A—B and A—B—A', B consists of a block of a conjugated diene, for example, butadiene, isoprene or pentadiene-1,3, and blocks A and A' consist of vinyl aromates, for example, styrene, alpha-methylstyrene, vinyl toluene, vinyl xylene and/or vinyl naphthalene. B preferably consists of polybutadiene and A and A' preferably consist of polystyrene. Radial teleblock copolymers are to be understood to mean branched polymers having blocks which are formed by a polymer of a conjugated diene, preferably butadiene, blocks of a vinyl aromatic compound, preferably styrene and a coupling agent. In this copolymer structure, various chains of the diene polymer, usually three or more, start from a coupling agent in which each chain at its other end comprises a block of the aromatic vinylpolymer. All the said block copolymers are known per se.

30 D. Polystyrene or rubber-modified polystyrene.

As a polystyrene there may be used a compound which contains more than 25% of units of a compound of the formula R—C(C₆H_(5-p)Z_p)=CH₂, wherein R is a hydrogen atom, a lower alkyl group (having, for example, 1–6 carbon atoms) or a halogen atom, Z is a hydrogen atom or a chlorine atom or a lower alkyl group or a vinyl group and p=0 or an integer from 1 to 5.

Suitable polystyrene compounds and suitable rubber-modified polystyrene compounds (high-impact polystyrene) are homopolymers, for example, polystyrene itself, polychlorostyrene and poly-alpha-methyl styrene, rubber-modified polystyrenes, for example, the commercially available high-impact polystyrene polymers and also the styrene-containing copolymers, for example, styrene acrylonitrile copolymers, styrene butadiene copolymers, styrene acrylonitrile-butadiene terpolymers, copolymers of ethylvinylbenzene and divinylbenzene and the like.

When the polymer mixture includes a polystyrene or a rubber-modified polystyrene, the ratio between the quantity by weight of polyphenylene ether and polystyrene may be varied within wide limits, for example, between 1:4 and 20:1.

45 E. Usual additives for polymer mixtures of polyphenylene ether.

Examples of usual additives are dyes and pigments, agents to make the polymer mixture antistatic, agents to give the polymer mixture better flame-retarding properties, stabilizers, fillers, reinforcing fibres and mineral oil.

The articles according to the invention are manufactured according to usual techniques of processing synthetic resins, for example, by injection moulding, extrusion and the like. Layers of lacquer or adhesive on the basis of a polyurethane may be provided on the articles. Lacquers on the basis of an alkyd/melamine system or epoxy adhesives may also be provided.

Polyurethane lacquers or adhesives are to be understood to mean lacquers or adhesives which comprise urethane groups in the ultimate protective layer or in the ultimately formed compound. Urethane groups are formed by the reaction of an active hydrogen atom of a hydroxyl group with an isocyanate group.

In most cases a polyurethane lacquer or adhesive consists of two components which are mixed with each other immediately before use. The two components are usually a prepolymer with isocyanate end groups and a resin with reactive OH-groups. In Verfkronek, 43 (1970), p. 269–276 are mentioned as examples of suitable reactive resins:

- a. polyacrylate-polylol
- b. polyester-polylol
- c. polyether-polylol

65 The OH-value of the lacquer or adhesive determines the ultimate degree of cross-linking of the lacquer

0 137 545

or adhesive. The lacquer or adhesive usually comprises one or more of the following solvents: ethyl acetate, butyl acetate, toluene and xylene.

Alkyd/melamine lacquers are baking enamels. By raising the temperature (baking), curing takes place. The two components, on the one hand the alkyd resin with free carboxyl groups and on the other hand the melamine resin with free OH-groups, are supplied as one system.

Suitable epoxy adhesives are two-components systems which are mixed immediately before use. The main component is an epoxy resin having a given epoxy equivalent number, while the second component, "the hardener", ensures curing by reaction with the epoxy group.

In the examples hereinafter, thin, disk-shaped plates are formed by injection moulding from the polymer mixtures mentioned therein. Lacquer layers and/or adhesive layers on the basis of a polyurethane are provided on said plates. The bonding between the polyurethane lacquer layer—if not otherwise stated—is determined according to the so-called "Gitterschnittprüfung von Anstrichen und ähnlichen Beschichtungen" (cross-cut test on paint coatings and similar coatings) according to DIN 53 151. The tests have been carried out with an Ericsen type 295 testing apparatus. By means of said testing apparatus, a pattern of squares is scratched in the coating layer. An adhesive tape is adhered across said pattern; the tape is thoroughly pressed on. The adhesive tape is then pulled off. The appearance of the square pattern is then evaluated visually. With an evaluation Gt0 the coating layer is still fully intact. With an evaluation Gt5 more than 65% of the surface of the diamond pattern has worked loose. With intermediate evaluations Gt1, Gt2, Gt3, Gt4 a result getting worse and worse in this sequence is obtained.

The bonding of the adhesive layer is determined as follows. A standardized tensile test bar is manufactured from the polymer mixtures by injection moulding. A PVC-foil is adhered to the tensile test bar by means of adhesive (example III). The adhesive is cured. The peel resistance is then determined (N/mm). The peel resistance is defined as the average force per length unit of the bonding line to further pull apart the two parts bonded together once the peeling has started. For this method of determining the peel resistance there may be referred to International Standard ISO 4578-1979 (E) and to DIN 53 282. In Example IV the bonding of the adhesive is determined by adhering two tensile test bars together with an overlap of 1 cm. The force necessary to slide the tensile test bars parallel to each other is then measured as the peel resistance (N/mm²).

30 Example I

Polymer mixtures were prepared (samples A, B and C) having a composition as stated in Table I hereinafter. From these mixtures, thin disc-shaped plates were manufactured by injection moulding. The plates were lacquered under different conditions with three commercially available polyurethane lacquers by means of a spray gun. The bonding between the plates and the lacquer layer was determined after seven days according to the "Gitterschnittprüfung" (cross-cut test) (DIN 53151). The lacquer conditions and the results obtained are recorded in Tables II, III, IV, V and VI herein after. The tests were always carried out in quintuplicate.

TABLE I

40	Sample	(composition parts by weight)		
		A	B	C
	Poly(2,6-dimethyl-1,4-phenylene ether)	44	40	53
	High-impact polystyrene	56	51	38
45	ZnO+ZnS	0.3	0.3	0.3
	Organic phosphite	0.7	0.7	0.7
	Block copolymer ¹	—	6.5	6.5
	Epoxy compound ²	—	2.5	2.5

50 ¹⁾ a block copolymer of the type A—B—A', wherein A and A' are polystyrene blocks and B is a non-hydrogenated polybutadiene block, obtainable under the trademark Cariflex TRKX-65

²⁾ an epoxy compound in the form of a solid epoxide resin on the basis of bisphenol A, obtainable under the trademark Araldit GT 7071.

55

60

65

0 137 545

TABLE II

Conditions upon spraying the polyurethane lacquer.

— distance spray gun-substrate	0.3 m
— pressure in spray gun	0.3 megapascal (MPa)
— temperature substrate	30°C
— curing lacquer	30 minutes at 80°C

Sample	Lacquer I ³	Lacquer II ⁴
A	1×GT4; 4×Gt0	5×Gt0
B	5×Gt0	5×Gt0
C	5×Gt0	5×Gt0

¹⁵) and ⁴⁾ see note below Table VI

TABLE III

Conditions upon spraying the polyurethane lacquer

— distance spray gun-substrate	0.6 m
— pressure in spray gun	0.4 megapascal (MPa)
— temperature substrate	30°C
— curing lacquer	30 minutes at 80°C

25	Results: Sample	Lacquer I ³	Lacquer II ⁴
	A	5×Gt4	1×Gt2; 4×Gt0
	B	5×Gt0	5×Gt0
	C	5×Gt0	5×Gt0

30 *Journal of Health Politics, Policy and Law*, Vol. 33, No. 2, March 2008

TABLE IV

TABLE IV

Conditions upon spraying the polyurethane lacquer	
— distance spray gun-substrate	0.6 m
— pressure in spray gun	0.4 megapascal (MPa)
— temperature substrate	20°C
— curing lacquer	30 minutes at 80°C

	Results: Sample	Lacquer I ³	Lacquer II ⁴
40	A	5xGt4	4xGt2
	B	5xGt4	5xGt0
45	C	5xGt4	5xGt0

³⁾ and ⁴⁾ see note below Table VI

TABLE V

Results: Sample	Lacquer I ³
A	5xGt0
B	5xGt0
C	5xGt0

³⁾ see note below Table VI

0 137 545

TABLE VI

Conditions upon spraying the polyurethane lacquer

— distance spray gun-substrate	0.6 m
— pressure in spray gun	0.6 megapascal (MPa)
— temperature substrate	35°C
— curing lacquer	30 minutes at 80°C

5

10

Results: Sample	Lacquer I ³	Lacquer II ⁴
A	5xGt4	4xGt2/3; 1xGt0
B	5xGt4	5xGt0
C	5xGt4	5xGt0

15 ³- Lacquer I is a two components polyacrylate-polyol/isocyanate having an OH-value of 4%, commercially available as "Autocryl" from Messrs. Sikkens.

4. Lacquer II is a two components polyacrylate-polyol/isocyanate lacquer having an OH-value of 4%, commercially available as "Cellioster 1834" from Messrs. La Celliose.

20 It appears from the Tables that the conditions upon spraying the lacquers are of importance for the resulting bonding. In practice, however, it is of essential importance that a good bonding should also be obtained in less optimum conditions.

It appears from the Tables that with the samples B and C according to the invention a better or equal result is obtained as with sample A (reference sample).

25

Example II.

Two polymer mixtures were prepared corresponding to samples A and B of Table I. Disk-shaped plates were manufactured from the polymer mixture by means of injection moulding. The plates were lacquered with a polyurethane lacquer under different conditions. As a polyurethane lacquer was used a two-components polyacrylatepolyol/isocyanate lacquer obtainable as "Cellioster 2400 Alu Nacre 3387 HU" from La Celliose.

All experiments were carried out in quintuplicate. The bonding strength was determined according to the "Gitterschnitt" test. Moreover the impact strength prior to and after painting was determined according to the so-called "falling dart impact" test (thickness disk 3.2 mm; falling height 2.15 m; mass 10.378 kg).

35 The results are recorded in Table VII.

40

45

50

55

60

65

0 137 545

TABLE VII
Sample A Sample B

5	Properties before painting "Falling dart impact strength" (J)	60	95
10	Condition used upon spraying the poly- urethane lacquer	"Gitterschnitt" value	"Gitterschnitt" value cross-cut
15	I distance spray gun- substrate 0.3 m; pressure in spray gun 0.3 mega- pascal; temperature surface 20°C; curing lacquer 30 min. at 80°C	5×Gt0	5×Gt0
20	II distance spray gun- substrate 0.6 m; pressure in spray gun 0.6 mega- pascal; temperature surface 20°C; curing lacquer 30 min.	1×Gt0 3×Gt2 1×Gt4	5×Gt0
25	at 80°C		
30	III distance spray gun- substrate 0.6 m; pressure in spray gun 0.6 mega- pascal; temperature surface 35°C; curing lacquer 30 min. at 80°C	5×Gt4	5×Gt0
35	Properties after painting according to II. "Falling dart impact strength" (J)	10	50

It may be seen from Table VII that sample B according to the invention shows a better or equal bonding
40 with polyurethane lacquer than sample A (reference sample).

Example III.

Three polymer mixtures were manufactured with the composition as stated hereinafter in Table VIII.

45 TABLE VIII
(Compositions in parts by weight)

	Sample	D	E	F
50	poly(2,6-dimethyl-1,4-phenylene ether)	32	32	32
	high-impact polystyrene	64	64	64
	ZnO+ZnS	0.3	0.3	0.3
	organic phosphite	0.9	0.9	0.9
	block copolymer ¹	5	5	5
55	epoxy compound ²	—	3	6

1¹ and 2²: In this example the same blockcopolymer and the same epoxy compound were used as indicated in Example I, Table I.

60 Standardized rods for a tensile test were manufactured from the resulting polymer mixtures by injection moulding. A PVC foil was adhered to the rods by means of a polyurethane adhesive, namely a two-components polyurethane adhesive of the tradename "Hernerts 7550". The glued joint was heated at 80°C for 5 minutes. After 5 days the peel resistance was determined. The results are recorded in Table IX
65 hereinafter.

0 137 545

TABLE IX

Sample

D

E

F

Average peel resistance (three measurements) N/mm	2.8±0.05 ^{a)}	3.6±0.1 ^{a)}	3.7±0.1 ^{a)}
---	------------------------	-----------------------	-----------------------

5

^{a)} Standard deviation.

Example IV.

10 A large number of tensile test bars were formed (injection moulded) from each of the polymer mixtures according to samples A, B and C of Example I. Always two rods from the same polymer mixture were bonded together with an overlap of 1 cm by means of a polyurethane adhesive or an epoxy adhesive. The adhesive was cured, partly at 20°C and partly at 80°C (60 minutes) and partly at 120°C (60 minutes). Two different polyurethane adhesives and one epoxy adhesive were used. Seven days after adhering the peel resistance was determined. Each test was repeated four times. The results obtained are recorded in Table X hereinafter.

15

TABLE X
Peel resistance (N/mm²) after curing at
20°C 80°C 120°C

20

Sample A

Adhesive I ⁵	3; 3; 3; 3	7; 7; 4; 4	—
Adhesive II ⁶	1; <1; <1; <1	3; 2; 1; 1	6; 6; 5; 4
Adhesive III ⁷	2; 2; 2; 1	2; 2; <1; <1	—

25

Sample B

Adhesive I ⁵	4; 3; 3; 2	7; 9; 3; 3	—
Adhesive II ⁶	3; 2; 2; 2	4; 3; 3; 3	4×10
Adhesive III ⁷	3; 3; 3; 2	8; 8; 8; 5	—

30

Sample C

Adhesive I ⁵	6; 5; 4; 4	>10; 10; 9; 4	—
Adhesive II ⁶	3; 3; 2; 2	6; 4; 4; 3	4×>10
Adhesive III ⁷	3; 3; 2; 2	4; 4; 4; 2	—

35

⁵⁾ A two-components polyurethane adhesive commercially available under the trademark Bison from Perfekta.⁶⁾ A two-components polyurethane adhesive commercially available under the trademark Macropласт UK 8210 from Henkel.

40

⁷⁾ A two-components epoxy adhesive commercially available under the indication "XB-7838 B/A from 3M Company.

It may be seen from the Table that the samples B and C according to the invention provide a better or equal peel resistance as compared with Sample A (not according to the invention).

45

Example V.

Polymer mixtures (samples G, H, J and K) were prepared in a composition as indicated in Table XI hereinafter. Injection moulding, lacquering and determination of bonding were carried out as stated in Example I. The results obtained are recorded in Table XII.

50

TABLE XI

(Composition parts by weight)

Sample

G

H

J

K

55

Poly(2,6-dimethyl-1,4-phenylene ether)	44	44	44	44
High-impact polystyrene	56	56	56	56
ZnO+ZnS	0.3	0.3	0.3	0.3
Organic phosphite	0.8	0.8	0.8	0.8
Block copolymer ¹	—	—	6.5	6.5
Epoxy compound ²	—	2.5	—	2.5

¹⁾ and ²⁾ see Table I.

65

0 137 545

TABLE XII
"Gitterschnitt" value

	Sample	G	H	J	K	
5	I Distance spray gun-substrate 0.45 m; pressure in spray gun=0.6 MPa; temperature substrate=35°C; curing lacquer 75 minutes at 80°C		4×Gt4	4×Gt0	4×Gt4	4×Gt0
10						
15	II Distance spray gun-substrate 0.6 m; pressure in spray gun=0.6 MPa; temperature substrate=20°C; curing 30 minutes at 120°C		2×Gt4	2×Gt0	2×Gt0	2×Gt0
20						
25	III Distance spray gun-substrate 0.6 m; pressure in spray gun=0.6 MPa; temperature substrate=20°C; curing lacquer 30 minutes at 80°C	3×Gt4	2×Gt4 1×Gt0	1×Gt4 2×Gt0	1×Gt4 2×Gt0	
30						

It appears from Table XII that under critical lacquer conditions the sample with the block copolymer shows a better or equal bonding than the reference sample, while the sample with only the epoxide compound shows a better bonding, and the sample with both the block copolymer and the epoxide compound shows the best bonding.

Example VI

Polymer mixtures were prepared having a composition as of sample A to which, however, 2.5 parts by weight of various epoxy compounds are added (Table XIII). The samples L, M, N and P were obtained in this manner (Table XIII). Injection moulding, lacquering and bonding determination were carried out as stated in Example I. The bonding found is recorded in Table XIV.

TABLE XIII
(Composition parts by weight)

	Sample	A	L	M	N	P
45	Epoxy compound:					
	Edenol B 35 ^a	—	2.5	—	—	—
50	Edenol D 81 ^b	—	—	2.5	—	—
	Edenol B 316 ^c	—	—	—	2.5	—
	ERL 4221 ^d	—	—	—	—	2.5

^a Edenol B 35 is an isoalkyl epoxystearate of Henkel

^b Edenol D 81 is an epoxidized soya bean oil of Henkel

^c Edenol B 316 is an epoxidized linseed oil of Henkel

^d ERL 4221 is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexyl carboxylate and is marketed by Union Carbide Corporation under the tradename Bakelite Cycloaliphatic Epoxy Resin ERL 4221

0 137 545

TABLE XIV

	Sample	A	L	M	N	P
5	I Distance spray gun-substrate =0.6 m; pressure in spray gun=0.6 MPa; temperature substrate=35°C; curing lacquer 30 minutes at 80°C.					
10		3×Gt4	3×Gt0	3×Gt0	3×Gt0	3×Gt0
15	II Distance spray gun-substrate =0.6 m; pressure in spray gun=0.6 MPa; temperature substrate=35°C; curing lacquer 30 minutes at 120°C.	3×Gt4	2×Gt0 1×Gt2	3×Gt0	2×Gt0 1×Gt2	3×Gt0
20						

Example VII.

25 Test plates were manufactured from polymer mixtures according to samples A and C of Example I. The samples were lacquered by spraying with two different alkyd/melamine lacquers. The conditions during lacquering and the found bonding results are recorded in Table XV hereinafter.

TABLE XV

	Sample	"Gitterschnitt" value	
		A	C
Conditions during lacquering			
30	— distance spray gun-substrate 0.3 m.		
35	— pressure in spray gun 0.3 MPa		
	— temperature substrate 20°C		
	— curing lacquer 30 minutes at 80°C		
40	Lacquer III ¹²	2×Gt4; 1×Gt0	3×Gt0
	Lacquer IV ¹³	3×Gt4	3×Gt4
45	Conditions during lacquering as above, but:		
	— curing lacquer 30 minutes at 120°C		
50	Lacquer III ¹²	3×Gt4	3×Gt0
	Lacquer IV ¹³	3×Gt4	2×Gt4;
Conditions during lacquering			
	— distance spray gun-substrate 0.6 m		
	— pressure in spray gun 0.6 MPa		
	— temperature substrate 20°C		
	— curing 80°C		
55	Lacquer III ¹²	3×Gt4	3×Gt0
	Lacquer IV ¹³	3×Gt4	3×Gt4
Conditions as above, but:			
	— curing 120°C		
60	Lacquer III ¹²	3×Gt4	3×Gt4
	Lacquer IV ¹³	3×Gt4	3×Gt4

¹²⁾ An alkyd/melamine paint having a rather high carboxyl value, obtainable under indication C3E577 from Schaeppman Lakfabrieken.

¹³⁾ An alkyd/melamine paint (code C4E34) having a free inorganic acid (code H4E15) of Schaeppman Lakfabrieken.

0 137 545

It may be seen from the results recorded in Table XV that a better or equal bonding is obtained with a polymer mixture according to the invention B than with polymer mixture A (reference sample).

Claims

5 1. An article manufactured from a polymer mixture comprising a polyphenylene ether, optionally a polystyrene or a rubber-modified polystyrene and comprising a lacquer layer or an adhesive, characterized in that the article is manufactured from a polymer mixture which comprises a polyphenylene ether and an epoxy compound.

10 2. An article as claimed in Claim 1, characterized in that the article is manufactured from a polymer mixture which comprises in addition a saturated or unsaturated block copolymer having blocks derived from a conjugated diene and from a vinyl aromatic compound.

15 3. An article as claimed in Claims 1—2, characterized in that the article is manufactured from a polymer mixture which, calculated with respect to the overall quantity of polyphenylene ether, optionally present polystyrene or rubber-modified polystyrene, optionally present block copolymer, comprises 0.2 to 7.5% by weight of epoxy compound and 0 to 25% by weight of block copolymer.

20 4. An article as claimed in Claims 1—3, characterized in that the article is manufactured from a polymer mixture which comprises an epoxy compound having a molecular weight of more than 1,000.

25 5. An article as claimed in Claims 1—4, characterized in that the article is manufactured from a polymer mixture which comprises a block copolymer having blocks derived from butadiene and from styrene the polybutadiene blocks of which may be fully or partly hydrogenated.

30 6. An article as claimed in Claims 1—5, characterized in that the article has a polyurethane- or alkyd/melamine lacquer layer or a polyurethane- or epoxy adhesive layer.

25 Patentansprüche

35 1. Gegenstand der aus einer Polymerischung hergestellt ist, welche ein Polyphenylenäther, gegebenenfalls ein Polystyrol oder ein gummi-modifiziertes Polystyrol enthält und der weiterhin eine Lackschicht oder eine Klebstoffsicht aufweist, dadurch gekennzeichnet, daß der Gegenstand aus einer Polymermischung hergestellt ist, die einen Polyphenylenäther und eine Epoxy-Verbindung enthält.

40 2. Gegenstand nach Anspruch 1, dadurch gekennzeichnet, daß er aus einer Polymermischung hergestellt ist, die zusätzlich ein gesättigtes oder ungesättigtes Blockcopolymer mit Blöcken aufweist, die von einem konjugierten Dien und von einer vinylaromatischen Verbindung abgeleitet sind.

45 3. Gegenstand nach den Ansprüchen 1 bis 2, dadurch gekennzeichnet, daß er aus einer Polymermischung hergestellt ist, die berechnet auf die Gesamtmenge an Polyphenylenäther, gegebenenfalls vorhandenes Polyphenylenäther, gegebenenfalls vorhandenes Polystyrol oder gummi-modifiziertes Polystyrol, gegebenenfalls vorhandenes Blockcopolymer, 0,2 bis 7,5 Gew.-% Epoxy-Verbindung und 0 bis 25 Gew.-% Blockcopolymer enthält.

50 4. Gegenstand nach den Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß er aus einer Polymermischung hergestellt ist, die eine Epoxy-Verbindung mit einem Molekulargewicht von mehr als 1000 aufweist.

55 5. Gegenstand nach den Ansprüchen 1 bis 4, dadurch gekennzeichnet, daß er aus einer Polymermischung hergestellt ist, die ein Blockcopolymer mit Blöcken enthält, die von Butadien und von Styrol abgeleitet sind und wovon die Polybutadienblöcke vollständig oder teilweise hydriert sein können.

60 6. Gegenstand nach den Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß er eine Polyurethan- oder Alkyd/Melamin-Lackschicht oder eine Polyurethan- oder Epoxy-Klebstoffsicht aufweist.

Revendications

50 1. Objet fabriqué à partir d'un mélange de polymères comprenant un poly(oxyphénylène), éventuellement un polystyrène ou un polystyrène modifié au caoutchouc et comprenant une couche de laque ou un adhésif, caractérisé en ce que l'objet est fabriqué à partir d'un mélange de polymères qui comprend un poly(oxyphénylène) et un composé époxy.

55 2. Objet selon la revendication 1, caractérisé en ce que l'objet est fabriqué à partir d'un mélange de polymères qui comprend en plus un copolymère séquencé saturé ou insaturé ayant des séquences dérivées d'un diène conjugué et d'un composé vinyl aromatique.

60 3. Objet selon les revendications 1—2, caractérisé en ce que l'objet est fabriqué à partir d'un mélange de polymères qui, calculé par rapport à la quantité totale de poly(oxyphénylène), de polystyrène ou de polystyrène modifié au caoutchouc éventuellement présent, de copolymère séquencé éventuellement présent, comprend de 0,2 à 7,5 pourcent en poids de composé époxy et de 0 à 25 pourcent en poids de copolymère séquencé.

65 4. Objet selon les revendications 1—3, caractérisé en ce que l'objet est fabriqué à partir d'un mélange de polymères qui comprend un composé époxy ayant une masse molaire supérieure à 1000.

65 5. Objet selon les revendications 1—4, caractérisé en ce que l'objet est fabriqué à partir d'un mélange

0 137 545

de polymères qui comprend un polymère séquencé ayant des séquences dérivées du butadiène et du styrène, dont les séquences polybutadiène peuvent être complètement ou partiellement hydrogénées.

6. Objet selon les revendications 1—5, caractérisé en ce que l'objet porte une couche de laque de polyuréthane ou de résine alkyde/mélamine ou une couche d'adhésif de polyuréthane ou de résine époxy.

10

15

20

25

30

35

40

45

50

55

60

65